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## ► To cite this version:

Morgan Almanza, A. Pasko, F. Mazaleyrat, Martino Lobue. First vs second order magnetocaloric material for thermomagnetic energy conversion. 2017 IEEE International Magnetism Conference (INTERMAG 2017), Apr 2017, Dublin, Ireland. 10.1109/INTMAG.2017.8007630 . hal-01790628

**HAL Id: hal-01790628**

**<https://hal.science/hal-01790628>**

Submitted on 13 May 2018

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# First vs second order magnetocaloric material for thermomagnetic energy conversion

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The supply of waste heat represents a huge and freely available amount of energy that make it a key target for energy conversion technologies, notwithstanding the small thermodynamic efficiency to be expected because of the limited working temperature difference. Energy harvesting systems from waste heat based on thermomagnetic generation (TMG) have been studied since the 1948 paper by Brillouin and Iskenderian [1]. The new generation of magnetocaloric materials (MCM) raised a renewed interest towards this technology [2]. Recently we published numerical simulations of isofield-isotemperature and adiabatic-isotemperature cycles in finite time thermodynamics [3] (i.e. where thermal exchange is taken into account in a non-quasistatic regime), allowing to estimate the efficiency at maximum power (EMP) using first and second order phase transition magnetocaloric materials as active substance. Our preliminary results made possible the comparison with thermoelectric generators [4], showing a similar power density for temperature span lower than 10°C, but a much higher relative efficiency from 0.05 to 0.2 in the case of thermomagnetic cycles. However, these cycles are still highly idealized ones as they assume a perfect control of their shape based on field feedback. Indeed, iso-temperature transformations used in [3] to work out best efficiencies can be hardly achieved in an actual device that would more easily work on a iso-field-adiabatic cycle (i.e. a Brayton cycle).

Here we shall show how the constitutive relation (i.e. the equation of state) of the material leads the actual shape of a finite time thermodynamic cycle. Our main result is to show that for first-order MCM the iso-field transformation stays closer to an iso-temperature one allowing a significant efficiency improvement with respect to second order MCM. Using the method presented in [3], we study the potential benefit of first order MCM in terms of power density and efficiency compared to the second order MCM for cycle with adiabatic and iso-field process. Results will also be compared with thermoelectric generator at maximum power [4].

## I. SYSTEM AND MATERIAL MODELING

Two approaches are commonly envisaged to harvest the magnetic energy produced by the cycling of the active material around a temperature induced ferromagnetic-paramagnetic transition. The first uses the magnetization change in time to drive an electric current [5] whereas the second uses the mechanical work associated with the difference of magnetic force due to a magnetization change [6]. Due design constraints, a thermodynamic cycle composed by two iso-field and two adiabatic processes (i.e. Brayton cycle), is the commonest choice for systems of the latter class. Here we compute the thermodynamic cycle following [3], namely using an equation of state, deduced from a phenomenological Landau model and

describing the heat exchange using a coefficient  $k_{high}$  of  $1 \text{ W} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$ .

## II. THERMODYNAMIC SIMULATION

Given the power density, the maximum relative efficiency  $\eta_{rel}$ , with respect to the Carnot efficient  $\eta_{Carnot}$ , is achieved by minimizing the entropy production  $s_i$ . Here we take into account only  $s_i$  associated with the finite-time heat exchange (i.e. hysteresis and kinetics associated with the magnetic transition are neglected). To do that we use a linear model of heat exchange where, as shown in [3], entropy production is minimum when heat exchange takes place at constant temperature difference (HECTD). This means that efficiency is maximum when the difference between the temperature  $T(t)$  of the reservoirs,  $T_{hot}$  or  $T_{cold}$ , respectively for the hot reservoir and the heat sink, are constant during the heat exchange process (that is why we use the term iso-temperature rather than isotherm to name this transformation).

Calculations of cycles, as shown in the Figure 1, with  $T_{hot} = 298 \text{ K}$ ,  $T_{cold} = 291 \text{ K}$  for first and second order MCM give for the small cycles,  $P_{mag} = 10 \text{ mW} \cdot \text{cm}^{-3}$ ,  $\eta_{rel} = 0.45$ ,  $t_{period} = 0.1 \text{ s}$  while for large cycle we have for first order  $P_{mag} = 9.2 \text{ mW} \cdot \text{cm}^{-3}$ ,  $\eta_{rel} = 0.41$ ,  $t_{period} = 10 \text{ s}$  and for second order  $P_{mag} = 8.2 \text{ mW} \cdot \text{cm}^{-3}$ ,  $\eta_{rel} = 0.41$ ,  $t_{period} = 10 \text{ s}$ . In the Figure 1 we show that first order MCMs in iso-field processes keep closer to a HECTD, during the transition, than second order MCM allowing to get closer to the optimum cycle. The difference is apparent comparing the low temperature iso-field line, in Figure 1, the first order material (red line) shows a horizontal line (a perfect iso-temperature transformation) whereas the second order one (black line) shows finite slope. Nevertheless, it is worth noting that both second and first order MCM can approach HECTD by drastically reducing the span of the iso-field process, as in the dashed line cycles in Figure 1. This means EMP for first and second order materials will be very similar when working on tiny cycles at a rather high frequency. In the Figure 2, we show the maximum power for different  $t_{period}$ , a slight increase of the power density for the first order MCM for longer periods is apparent.

Small period cycles are expected to be achievable only in the case of micro-systems where fast switching can be achieved. However, high frequency excitation will very possibly increase the role of transition kinetics (neglected in our approach) in the case of first-order MCM. Thus we can conclude that, while first order materials are better suited for bulk applications, high-frequency micro-systems will be more efficiently designed using second order materials.

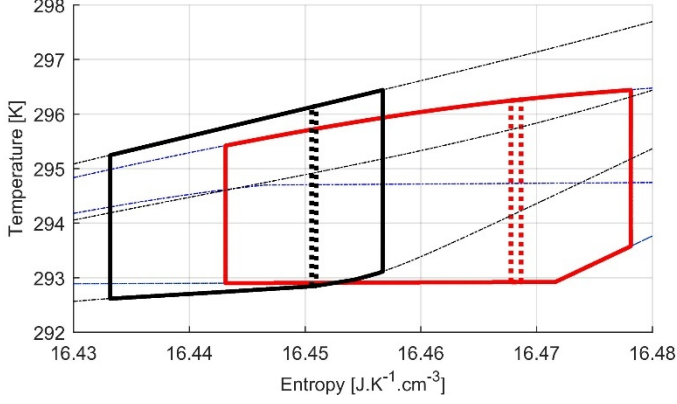


Figure 1 Brayton cycles on T-S diagram for the second order MCM (black) on the left and the first order MCM (red) on the right for large (full line) and small cycles (dotted line). Thin lines represent three isofields in black for second order and in blue for first order MCM.

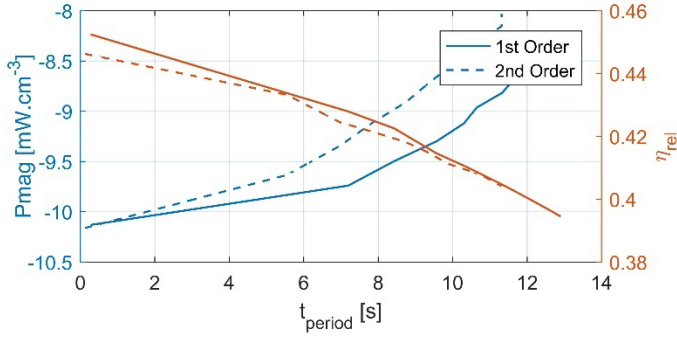


Figure 2 Maximum magnetic power and its relative efficiency for different time periods for first order in full line ( $H_{\text{applied}} = 0.67 \text{ T}$ ,  $\max(\Delta T_{\text{adia}}) = 3.4 \text{ K}$ ) and for second order in dashed line ( $H_{\text{applied}} = 1 \text{ T}$ ,  $\max(\Delta T_{\text{adia}}) = 3.4 \text{ K}$ ).

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